



# Transport Studies of Hydrogels Based on Natural Rubber and Polyethylene Oxide in Cationic Dye Solutions

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## Abstract

Block copolymers (BCs) of varying compositions were prepared from hydroxyl terminated liquid natural rubber (HTNR) and polyethylene oxide (PEO) of various molecular weight. The hydrophilic PEO enables these NR-b-PEO BCs to swell in water and in aqueous cationic dyes, viz., malachite green (MG), crystal violet (CV), safraninT (ST), methylene blue (MB) and bromocresol green (BCG). The diffusion and permeation coefficients of BCs increases with the PEO content. The swelling studies also point to the fact that the general order of interaction of the dyes with the BCs is  $MG > CV > ST > MB > BCG$ . The diffusional exponent value is Fickian in water and in dye solution for BC-1 and for the rest of the BCs it is of the anomalous type, with a bias towards the Fickian type. Hence it is inferred that the polymer relaxation rate is greater than the solvent diffusion rate in BC-1 during swelling whereas in the others, rate of polymer chain relaxation and the solvent diffusion rate are about the same order of magnitude.

**Keywords:** Natural rubber, polyethylene oxide, block copolymers, hydrogels, cationic dyes and self- assembling systems.

## Introduction

The important applications of hydrogels in various fields such as membranes in water purification and separation, catheters, contact lenses, agriculture, food industry, medicine and biotechnology<sup>1-2</sup> has generated considerable interest and attention in recent years, offsetting the exploration of the mechanism of solute diffusion. They are used as adsorbents for removal of some agents in environmental applications, in immobilized enzyme kinetics, in bioengineering and also in transportation of water, pesticides and fertilizers in agriculture<sup>3-9</sup>, which can lead to compromise in mechanical property of the hydrogels. Thus to control the water uptake, the general trend followed is affecting improvement of mechanical properties by controlling the chemical and physical crosslinking. It has been indicated that clusters of hydrophobic groups in a predominantly hydrophilic network or vice-versa may serve to increase load bearing without causing embrittlements or pliability respectively. Hydrophobic groups have been introduced by copolymerization of various hydrophobic monomers with hydrophilic monomers such as acrylamide 2- vinyl -N-pyrrolidone and 2-hydroxy ethylmethacrylate<sup>10-13</sup>.

Development of new polymeric materials, from renewable natural resources in our laboratory has led to the synthesis of block copolymers based on natural rubber and polyethylene oxide (PEO). They were found to be highly phase separated systems which can imbibe large quantities of water owing to the hydrophilic character of PEO, giving rise to excellent hydrogels. As the hydrophilic component was increased the samples became more plastic in nature and equilibrium swelling rose from 6% to 450% across the series of NR-b-PEO-2000, NR-b-

PEO-4000, NR-b-PEO-6000, NR-b-PEO-8000 and NR-b-PEO-10000. The present work envisages synthesis of the above mentioned BCs and verifying their swelling abilities and transport properties of the series of NR-b-PEO block copolymers in cationic dyes, viz., malachite green (MG), crystal violet (CV), safraninT (ST), methylene blue (MB) and bromocresol green (BCG). Sorption studies of NR-b-PEO hydrogels were undertaken with the view to arrive at useful information regarding mechanism of diffusion and efficiency of sorption and permeation of the cationic dyes in these hydrogels.

## Material and Methods

**Materials:** Natural crumb rubber (ISNR – 3L) supplied by Rubber Research Institute of India, Kottayam, Kerala was used for making all the natural rubber (NR) derivatives in the present study. Hydrogen peroxide (30% w/v, E-Merck, India) was used without purification. Toluene (E-Merck, India) was used as solvent without further purification. Toluene diisocyanate (TDI) (80/20 mixture of 2, 4- and 2, 6- isomers, Aldrich) was used as received.

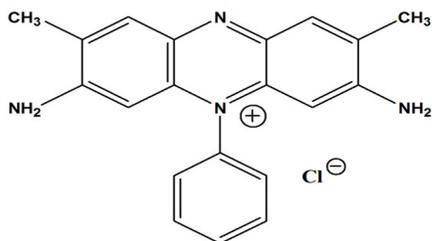
Polyethylene oxide or polyethylene glycol of different molecular weights ( $\bar{M}_n$ ), viz., 2000, 4000, 6000 (SISCO Research Laboratory), 8000 (Acros Organics, USA) and 10000 (Acros Organics, USA) were used as received. Safranin – T dye (National Chemicals, India) was recrystallised twice from ethanol - water medium. Malachite green, methylene blue, bromocresol green and crystal violet (E. Merck, India) were used as such without further purification. The chemical formulae and properties of the dyes are given in figure-1. The

PEOs were dried in vacuum oven below their melting point before using in synthesis.

Dibutyl tin dilaurate (DBTDL, Merck, India) was used as catalyst without further purification. Chloroform and methanol (Qualigens, India, synthetic grade) were used as such. Double distilled water was used for the preparation of dye solutions.

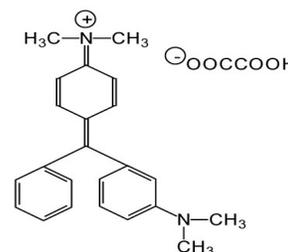
**Synthesis of NR/ PEO Block Copolymer:** The synthesis of these BCs were conducted by dissolving HTNR<sup>14,15</sup>, of number average molecular weight ( $\bar{M}_n$ ) 4700, in chloroform (23% w/v), adding Dibutyl tin dilaurate catalyst (0.3 % by wt of HTNR),

refluxing with stirring in atmosphere nitrogen, followed by dropwise addition of stoichiometric amount of TDI. Subsequently required amount of PEO was added dropwise, as a solution in chloroform (23% w/v) over a period of 1.5 hrs followed by 2 hrs stirring. Excess chloroform was distilled off and the viscous polymer was cast in trays treated with silicone releasing agent. The sheet was dislodged easily, after 12 hrs, kept in a vacuum oven at 60°C for complete removal of solvent present and then cured at 70°C for 24 hrs, followed by one week ageing at room temperature in a dry atmosphere. The overall compositions of the block copolymers prepared from HTNR, TDI and PEO in the molar ratio of 1:2.1:1.



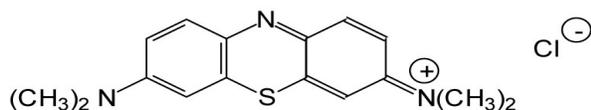
SafraninT

**Molar mass (gmol<sup>-1</sup>) 350.85**



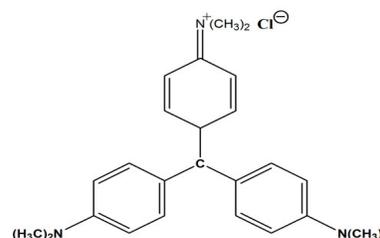
Malachite Green

**Molar mass (gmol<sup>-1</sup>) 419.51**



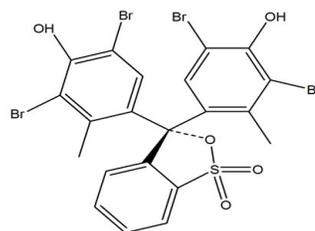
Methylene Blue

**Molar mass (gmol<sup>-1</sup>) 374**



Crystal violet

**Molar mass (gmol<sup>-1</sup>) 407.99**



Bromocresol green

**Molar mass (gmol<sup>-1</sup>) 698**

Figure-1

Chemical formulae and some properties of dyes

**Polymer designation:** The block copolymer prepared from HTNR and PEO-2000, viz., NR-b-PEO 2000 is denoted as BC-1. The complexes formed between BC-1 and methylene blue (MB) is indicated as BC-1.MB, between BC-1 and safranin T (ST) as BC-1.ST, between BC-1 and malachite green (MG) as BC-1.MG, between BC-1 and crystal violet (CV), between BC-1 and bromocresol green (BCG) as BC-1.BCG. The same designation has been adopted for the other virgin BCs and dye-stained BCs where BC-2, BC-3, BC-4, BC-5 were used to designate NR-b-PEO 4000, NR-b-PEO 6000, NR-b-PEO 8000 and NR-b-PEO 10000 respectively.

**Measurements: Swelling studies:** The swelling behaviour of dried BC-1 was studied by taking a disc of known mass ( $m_0$ ) and thickness and immersed into 30 ml water, maintained at  $30 \pm 0.10^\circ\text{C}$ . The water uptake with respect to time was obtained by periodically removing the sample from water, quickly blotting dry, reweighing and replaced into water. The swollen gels were weighed on an electronic balance (Kern,  $d=0.1\text{mg/cc}$ ). In a similar manner discs of BC-1 were placed in 30 ml aqueous solution of malachite green, safranin T, methylene blue, crystal violet and bromocresol green, each of concentration of  $2.0 \times 10^{-5} \text{ m/dm}^{-3}$  and the amount of solvent and dye adsorbed were measured gravimetrically, to generate six sets of swelling data (in water, MG, ST, CV, MB and BCG solutions). The measurements were continued until a constant weight was reached for each sample. Percentage of swelling of each hydrogel was calculated from the following relation

$$S\% = \frac{(m_t - m_0)}{m_0} \times 100 \quad (1)$$

where  $m_t$  is the mass of the swollen gel at time t, and  $m_0$  is the initial mass of the gel. Swelling studies of BC-2, BC-3, BC-4 and BC-5 were done on similar lines in water, MG, ST, CV, MB and BCG solutions

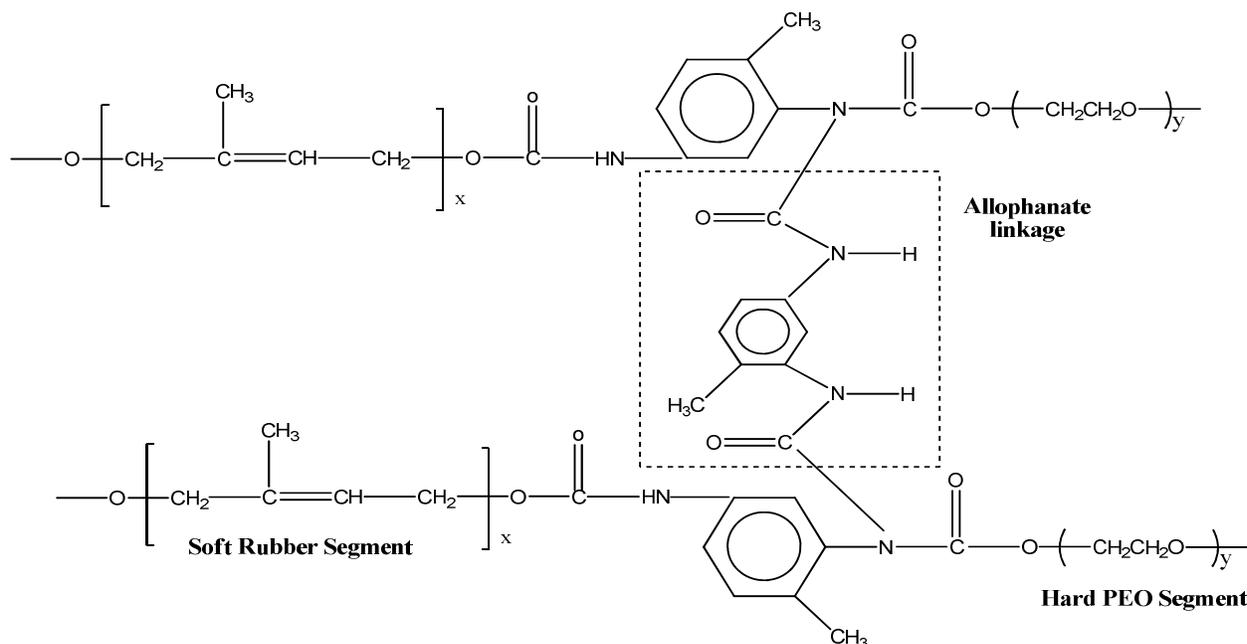
## Results and Discussion

**Synthesis:** PEO immobilised on NR was prepared as block copolymers in five different compositions, viz, BC-1 to BC -5 by varying the PEO molecular weight. The block copolymer structure and the allophanate linkage of these materials are shown in scheme 1.

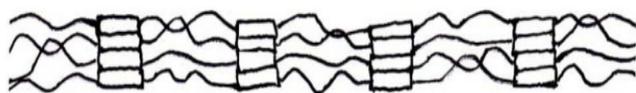
Cast sheets were honey coloured and on curing and ageing BC-3, BC-4 and BC-5 developed into firm sheets (plastics) where as BC-1 and BC-2 acquired more flexible characteristics showing elastomeric properties. As the amount of NR keeps of decreasing, and PEO content keeps on increasing the elastomeric nature of this materials changes to that of plastics.

**Swelling studies:** Transport properties through the BCs are interesting due to their two phase morphology, which is caused by nonpolar, 'soft', amorphous, rubbery segments and polar 'hard' glassy crystalline PEO segments.

The aggregate of the hard segments, which can be considered as junction points in a network of flexible molecules, the allophanate linkages and the hydrophilic nature of PEO endows upon these materials unique properties of hydrogels (scheme 2).



**Scheme-1**  
**Block copolymer structure and allophanate linkage**



**Virtually crosslinked extended network of polymer chains**



**Polymer Primary Chain**

**Scheme-2**

**Schematic illustration of the formation of hard segments as junction points**

The gradation in the size of the swollen hydrogels in water and the aqueous solution of the dyes can be attributed to the varying molecular weight and the ethylene oxide monomeric units of PEO table 1.

Swelling studies of BC-1 were conducted in water, MG, CV, ST, MB and BCG, the data was used in (1) to arrive at the values that help in drawing the swelling isotherm and arriving at the equilibrium swelling of BC-1 in water and the five dyes. Similar swelling studies were conducted with BC-2, BC-3, BC-

4 and BC-5 in the above mentioned medium and the molecular parameter datas are summarised in table 2.

The block copolymers have cross-linked network structure as evidenced from their interaction with water. The intermolecular allophanate linkages formed between the >NH of the urethane groups along the BC chains as shown in scheme 1 act as the crosslinks. Besides other physical forces such as intermolecular dipole interaction, hydrogen bonding also serves as cross-links. The chemical crosslinks decrease as the PEO chain length increases. Swelling studies yielded these values which are tabulated in table 2 along with other molecular parameters. BC-1 has more such chemical cross-links compared to BC-5.

In water and aqueous solution the lamellar biphasic morphology in the solid state of the BCs transforms to the core-shell conformation due to difference in solubility of the NR and PEO phase in water. The hydrophobic NR forms the core and the hydrophilic PEO forms the shell. As the shell is formed, the helical chains of PEO, relaxes but the allophanate linkages, hydrogen bonding and other physical forces operate to create a mesh in the PEO matrix. Since the number of EO units is least, viz., 45.4 in BC-1, it will have the highest cross-link density and hence the lowest average molar mass between cross-links ( $\overline{M_c}$ ) (table 2). On progressing across the series the

**Table-1**  
**Parameters associated with equilibrium swelling of NR-b-PEO block copolymers**

Sample	Time required to reach equilibrium swelling (days)	Dimensions (diameter) of swollen NR/PEO block copolymers (cm)					
		Water	MG	ST	MB	CV	VCG
BC-1	4	1.5	1.5	1.5	1.5	1.5	1.5
BC-2	4	2.0	2.0	2.0	2.0	2.0	2.0
BC-3	4	2.0	2.0	2.0	2.0	2.0	2.0
BC-4	2	2.3	2.3	2.3	2.3	2.3	2.3
BC-5	2	2.7	2.7	2.7	2.7	2.7	2.7

**Table-2**  
**Characteristic molecular parameters for the NR/PEO block copolymers**

Sample	N	$\overline{M_c}$	$v \times 10^{-3}$	$\rho_p$
BC-1	45.4	42.95	23.2	1.015
BC-2	90.8	224.28	4.45	1.036
BC-3	136.7	299.52	3.34	1.056
BC-4	181.1	637.68	1.56	1.135
BC-5	277.2	4883.0	2.00	1.241

Composition varies due to the increasing PEO content. Hence the dimension of the shells is of the following order BC-1 < BC-2 < BC-3 < BC-4 < BC-5. The frequency of allophanate linkage and other physical forces of cross-linking would also decrease across the series from BC-1 ( $23.2 \times 10^{-3}$ ) to BC-5 ( $2.0 \times 10^{-3}$ ). Thus the mesh size would gradually increase from BC-1 to BC-5 which is reflected in the lowest  $\overline{M}_c$  value of 42.95 for BC-1 and the highest  $\overline{M}_c$  value of 4883 for BC-5. Hence it can be surmised that, as the composition of BCs changes from BC-1 to BC-5, the mesh size increases across the series due to an increase in the number of ethylene oxide (EO) units and the molecular mass between cross-links and a corresponding decrease in cross-link density.

On immersing the BCs into water the lamellar morphology would transform into a three dimensional core-shell array comprising of NR cores enwrapped within shells of PEO (scheme 3)<sup>16</sup>. In other words there is a three dimensional expansion of the matrix as the hydrophilic PEO chains expand and relax in all five BCs. This kind of this self-assembly explains the enhancement in thickness of the BC samples on swelling. Yet another feature that we could conceptualise is that as we traverse the series, the NR cores in all the members would be of approximately the same size but the PEO corona would progressively increase in size from BC-1 to BC-5. This could be attributed to the increase in the number of EO units, viz., 45, 90, 136, 181 and 227 in BC-1, BC-2, BC-3, BC-4, BC-5 respectively.

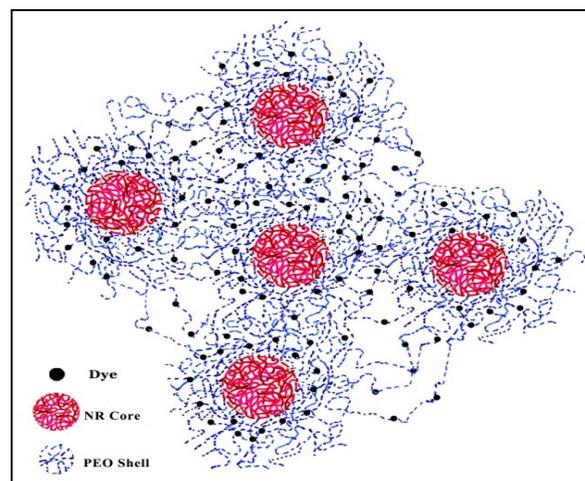
All the samples were extracted with distilled water before subjecting to swelling studies in order to remove any unbound PEO present in the sample. The dried samples were kept in the respective dye solution to attain equilibrium swelling. Percentage swelling was calculated using the relation

$$S\% = \frac{(m_t - m_0)}{m_0} \times 100 \quad (1)$$

where  $m_t$  is the mass of the swollen gel at time t and  $m_0$  is the mass of the dry gel.

Swelling studies of BC-1 were conducted in water, MG, CV, ST, MB and BCG, the data was used in Equation (1) to arrive at the swelling isotherm and the equilibrium swelling of BC-1 in water and the five dyes. Similar swelling studies were conducted with

BC-2, BC-3, BC-4 and BC-5 in the above mentioned medium and swelling isotherms were plotted for the dye solutions as shown in figure-2.



Scheme-3

A schematic representation of the core – shell array the BCs assume in aqueous dye solution

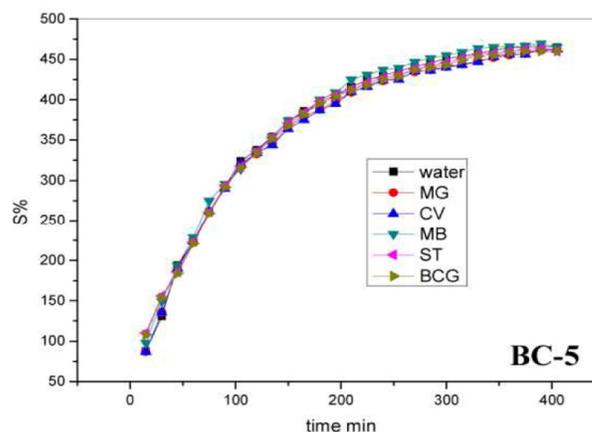


Figure-2

Swelling isotherms of the block copolymers  
 In all cases percentage swelling increases with time to reach a constant value which is the equilibrium swelling (table 3)

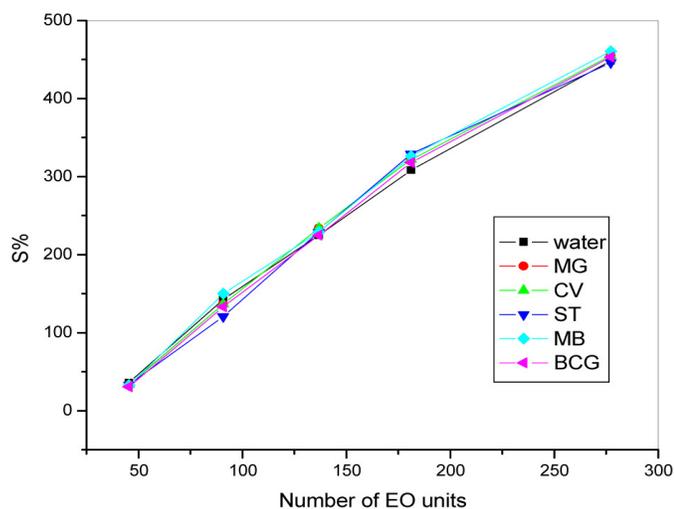
Table-3  
 Equilibrium uptake of water and the five dyes by block copolymers

Sample	Wt % of PEO	$S_{\infty} \%$					
		water	MG	ST	MB	CV	BCG
BC-1	29.8	5.6	6.5	5.8	5.7	6.49	5.5
BC-2	45.9	194	210	208	198	194	190
BC-3	56.0	225	237	228.8	229	234	225
BC-4	62.9	308	331.19	329	326	322	318
BC-5	67.9	448	450.88	446	460.70	455.16	453.2

The values of equilibrium swelling percentage in all the five dye solutions increase with PEO content, in the block copolymer. This is consistent with the degree of cross linking estimated in the respective sample (table 2). As the PEO content increases in samples from BC-1 to BC-5, the frequency of occurrence of the urethane linkage decreases, thereby decreasing the feasibility of the allophanate linkage. Hence the crosslink density decreases from BC-1 to BC-5. Lesser the crosslink and greater the  $\overline{M}_c$ , greater will be the space in the mesh created, facilitating the influx of water and the dye molecules along. Presence of water causes further chain relaxation and flexibility of the network conforming to the core-shell model and leading to greater ease of influx of the dye solution. Larger PEO chains facilitate the above process to a greater extent thereby helping to attain equilibrium swelling quickly (table 1). The equilibrium fluid content (EFC) of the dye solution in the gels have been calculated from the equation.

$$EFC = \frac{m_t - m_0}{m_0} \quad (2)$$

where  $m_t$  is the mass of the swollen gel at time  $t$  and  $m_0$  is the mass of the dry gel at zero time. The above results show that the higher values are observed for dye solutions compared to those in water and also the difference is large where the segment length of PEO becomes higher. From this it is obvious that dye molecules facilitate the entry of water molecules into the network and the process accelerates with the PEO content. This is explained on the basis of hydrogen bonds formed by the O and the N atoms present in the dye with water molecules. Thus more water is brought into the gel, as the number of EO monomeric units of the respective PEO segment increases. This view is supported by the plot given in figure-3.



**Figure-3**  
 Variation of equilibrium swelling with the number of monomeric units Sorption mechanism

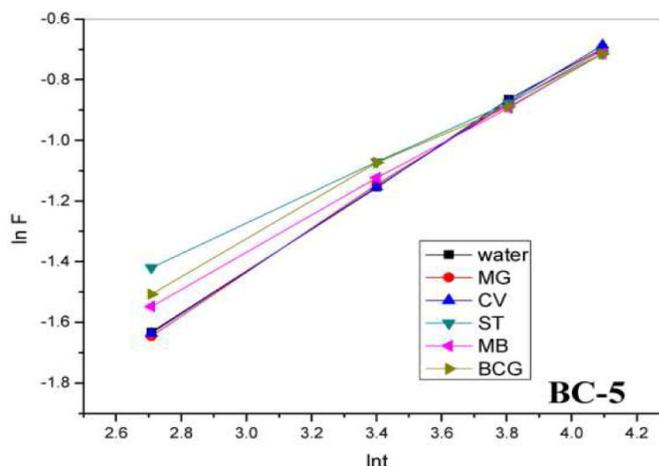
The dynamically formed spaces between the block copolymer chain by large scale segmental motion, leads to higher

separation between the chains, which determine the values of diffusion coefficient, sorption coefficient and permeation coefficients. This is revealed by the analysis of the mechanism of transport in the swellable polymeric system with the help of equation (3)

$$F = \frac{M_t}{M_\infty} = kt^n \quad (3)$$

where  $M_t$  and  $M_\infty$  denote the amount of solvent diffused into the gel at time  $t$ , 'k' is a constant characteristic of the network system and the penetrant and  $n$  is the diffusional exponent which is indicative of the transport mechanism. This equation is valid for the first 60% of the normalised solvent uptake. The parameter 'k' and 'n' were determined from a least square fit of the experimental  $\ln F$  versus  $\ln t$  plot (figure-4) and the values are tabulated in table 4. When the value of  $n$  is upto 0.5, the sorption mechanism is Fickian which indicates that the rate of the polymer chain relaxation is higher than the diffusion rate of the penetrant. When  $n=1$  and above the diffusion mechanism is said to be non-Fickian (Case II) where the rate of polymer chain relaxation is lower than the rates of diffusion. As the values of  $n$  lie in the range between 0.5 and 1.00 the system is said to be non-Fickian (anomalous) at which the rates of chain relaxation and diffusion are about the same order of magnitude.

It is clearly seen from table 5 that the value of diffusional exponent,  $n$ , ranges from 0.31 to 0.66. The diffusional exponent value is Fickian in water and in dye solution for BC-1 and for the rest of the BCs it is anomalous in water and in dye solutions. Hence it is inferred that the chain relaxation rate is greater than rate of diffusion of diffusant and solvent, in BC-1, during swelling in water and aqueous solution. This seems to be the trend in diffusion of ST into BC-2 and BC-3. In all other cases  $n$  is between 0.5 and 1.0 showing anomalous nature.



**Figure-4**  
 Swelling kinetic curves of the block copolymers

**Table-4**  
**Swelling exponents (n) and swelling constants (k) of the BCs in dye solutions**

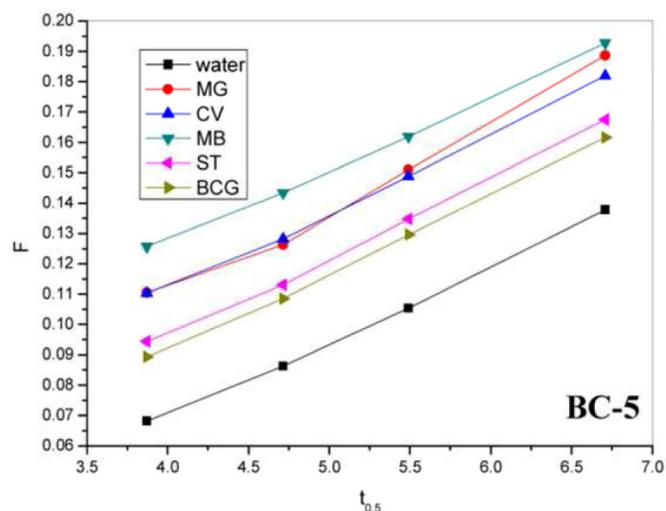
BC	kx10 <sup>-2</sup>						n					
	water	MG	ST	MB	CV	BCG	water	MG	ST	MB	CV	BCG
BC-1	1.87	1.47	1.40	1.53	3.11	5.22	0.40	0.33	0.32	0.31	0.43	0.19
BC-2	5.62	3.98	9.60	2.29	4.38	1.43	0.61	0.53	0.50	0.52	0.55	0.52
BC-3	6.81	10.44	13.63	10.15	8.43	6.61	0.60	0.61	0.50	0.51	0.58	0.54
BC-4	3.22	2.77	2.27	3.49	7.71	5.15	0.56	0.54	0.55	0.53	0.55	0.52
BC-5	2.93	2.96	5.85	3.87	6.97	4.28	0.66	0.65	0.54	0.60	0.60	0.66

The above data could be explained on the basis of the morphology of the polymer, the nature of the diffusants and solvent, obstruction by polymer network, the thermodynamic agitation and the hydrodynamic interaction. In the undissolved state, the NR segments which are trapped in the neighbouring crystalline lamellae of the lamellar, biphasic BC matrix would have mobility at room temperature, but the crystallites of PEO will not be mobile. When the BCs are introduced into water or aqueous solution the polar nature of water causes the lamellar, biphasic microdomain to assume a three dimensional core-shell arrangement, retaining the biphasic microdomain. Within the tight hydrophobic core at room temperature the NR segments have mobility. The crystalline domains of PEO will be transformed into the shell due to interaction with the water which overcomes the intramolecular forces of interaction but the allophanate linkages remain intact, thereby retaining the cross-links. Partial disruption of intermolecular attractive forces causes the PEO segments to develop segmental mobility and form the coronas. Hence in aqueous phase both the components have segmental mobility. The interaction of water and dye molecules is confined to the PEO domains. On visualization of the array of core-shell conformation in different block copolymers, the NR cores would be dominant relative to PEO cores in BC-1. As we proceed across the series from BC-1 to BC-5, the surface area of the PEO coronas would be expected to be the dominant morphological feature relative to the contracted cores. So polymer relaxation rate of both the segments, in the swollen state of BCs, in water or aqueous dye is appreciable in all the BCs but in BC-1 the predominant NR domain would be a hindrance and would reduce the diffusion rate. This explains the Fickian diffusion (n=0.5 or less) of BC-1. In all other cases polymer relaxation rate is appreciable, but as we traverse the series from BC-2 to BC-5 the mesh size due to cross - links in PEO would increase thereby causing the diffusion rate to increase and come on par with the polymer chain relaxation rate, viz., the anomalous type of diffusion (n is between 0.5 and 1.0) as in BC-2, BC-3, BC-4 and BC-5.

For all other BCs, viz., BC-2, BC-3, BC-4 and BC-5 the rate of segmental mobility is appreciable and as the mesh size increases the diffusion rate of dyes and water gradually increases across the series, although not equivalent to rate of segmental mobility. Hence there is bias towards Fickian. For example, the range of n in BC-2 is 0.5 to 0.55, in BC-3 is 0.5 to 0.6, in BC-4 is 0.52 to 0.56 and in BC-5 is 0.56 to 0.66. The diffusion of water in all

dyes is of the anomalous type due to the ease of entry and diffusion of small water molecules.

**Transport coefficients (D, S, and P):** The transport of solvents and solute through polymer materials has become the subject of several studies and a great deal of attention has been paid to swelling, diffusion, sorption and permeation.



**Figure-5**  
**Diffusion curves of the block copolymers**

**Diffusion Coefficient:** The diffusion coefficient is a kinetic parameter related to the polymer morphology, segmental mobility, penetrant nature and to the cross-links present in a polymer. It is generally determined from the slope of the linear portion (upto 60% equilibrium) of the swelling isotherm curve. Among the different methods short-time approximation method is generally used for the calculation of diffusion coefficients of hydrogels.

$$F = 4 \left[ \frac{Dt}{\Pi r^2} \right]^{1/2} - \Pi \left[ \frac{Dt}{\Pi r^2} \right] - \frac{\Pi}{3} \left[ \frac{Dt}{\Pi r^2} \right]^{3/2} \quad (4)$$

Where D is the diffusion coefficient (cm<sup>2</sup> min<sup>-1</sup>), t is the time (min), r is the radius of circular disc of the polymer samples. The comparison of Eqns (3) and (4) shows that the semi-empirical Equations (3) is obtained with n=0.50 and k=4[D/Π r<sup>2</sup>]<sup>1/2</sup>.

**Table-5**  
**Parameters for diffusion of NR/PEO block copolymers**

Adsorbent	$D \times 10^{-4} \text{cm}^2 \text{min}^{-1}$				
	BC-1	BC-2	BC-3	BC-4	BC-5
Water	1.68	48.68	51.19	61.65	439.8
MG	1.59	46.92	50.05	56.82	438.6
CV	1.50	45.05	48.55	55.15	432.9
MB	1.35	44.33	44.17	47.02	384.55
ST	1.40	50.77	47.06	53.97	415.40
BCG	1.29	43.00	43.0	45.0	380.55

The diffusion coefficients of the series of five NR-b-PEO hydrogels were calculated from the slope (k) of the lines obtained by the plot of F against  $t^{1/2}$  by a computational program in the five dye solutions of MG, ST, CV, BCG and MB (figure-5) and the value are shown in table 5.

Table 5 depicts the following trends (a) diffusion of water and the dyes into BC-5 > BC-4 > BC-3 > BC-2 > BC-1, (b) in general the diffusivity of water > MG > CV > ST > MB > BCG in the BCs.

The first observation can be understood in terms of the morphology, segmental mobility and cross-links of the BCs. When immersed in water PEO segments are solvated, causing relaxation through disentanglement, the allophante linkage however remains intact, thus retaining the mesh structure of the polymer matrix. Simultaneously the hydrophobic NR segments repel water and agglomerate to form a very tight core with coronas of PEO segments around them. The PEO segments retain cross-links, and relax to form coronas. This additional, dynamically created pore size in the corona also favours diffusion of the penetrants. The self assembly of the biphasic BCs into morphology of a three-dimensional core - shell array (scheme 3) causes the mesh size to increase in the PEO shell from BC-1 to BC-5, since  $\overline{M}_c$  increases from BC-1 – BC-5. The influx of dye and water molecules thus increases from BC-1 to BC-5.

Second observation can be assigned to the nature of the penetrant and polymer –dye interaction. Smaller molecular size and mass of water relative to the dyes renders it easy for the smaller and lighter water molecules to move faster. Dye molecules would be comprised of solvated anionic and cationic pairs which would be relatively heavier and thus mobility and diffusivity would be less.

MG, CV and BCG are triphenyl methane dyes. The cationic species of MG is the lightest of the above three (molar mass of cationic species of MG, CV and BCG are 330, 372.5 and 698 respectively). Hence the order of diffusivity is MG > CV > BCG. The molar mass of ST, viz., 315.35 which is the lightest would be expected to diffuse fast but the molecular geometry of diazine ring with phenyl group attached to it causes steric hindrance and hence would be expected to have a lower diffusivity than MG and CV. However, the diffusivity of ST would be expected to be more than BCG. The higher molar mass of the cationic species of MB, viz., 388.5 may be expected to cause lower diffusion than ST. But

it has a compact structure and hence would have lesser molecular diameter than ST. So the tendency of lower diffusion coefficient is compensated by lack of steric hindrance. Thus ST and MB's result may be comparable. Hence diffusion of MB expected to lesser than ST. The lowest diffusivity of BCG could be added to the highest molecular mass of 698. Closely associated sulphonate anion which is intramolecularly attached also hinders approach to ethereal oxygen.

**Sorption Coefficient:** It is calculated according to equation 5.

$$S = \frac{M_{\infty}}{M_0} \quad (5)$$

where  $M_{\infty}$  is the mass of the solvent at equilibrium swelling and  $M_0$  is the mass of the polymer sample. The sorption coefficient is thermodynamic in nature and is related to the equilibrium sorption of the penetrant.

The value of S helps in gauging the strength of interaction between polymer and penetrants. Table 6 shows the general trend of sorption coefficients which is MG > CV > MB > ST > BCG > water r, in each of the BCs. The lowest value of S of BCG could be ascribed to the proximity of the sulphonyl group, which forms a closely associated ion pair in aqueous solution, thereby hindering approach to the ethereal oxygen of PEO for CTC formation. A similar steric obstruction occurs in ST. Hence the extent of interaction of the bound dye is lesser in ST and BCG which is reflected in their sorption coefficient.

The above sequence could also be additionally supported in the light of the resonance stabilization, geometry of the dye molecules and the nature of interaction of the cationic dye with PEO part. MG and CV is a triphenylmethane dye, in which the cation is more resonance stabilized compared to the cationic azine ring in safranin T and the cationic thiazine ring in methylene blue. MG and CV may be expected to form CTC more readily than ST and MB. The CTC formation may be considered as a reversible sticky collision between the cationic dyes and ethereal oxygen, wherein the stronger ionic forces between the cation dye and the counteranion is not disrupted. Acquated dye cation and anion (chloride in ST and MB, oxalate in MG), i.e., the solvated ion pair can be visualized as approaching the ether linkages.

**Table-6**  
**Parameters for sorption coefficients of NR/PEO block copolymers**

Adsorbent	S g g <sup>-1</sup>				
	BC-1	BC-2	BC-3	BC-4	BC-5
Water	0.36	1.43	1.585	2.982	4.483
MG	0.34	1.23	1.627	3.301	4.508
CV	0.36	1.33	1.643	3.335	4.511
MB	0.38	1.37	1.683	3.72	4.551
ST	0.38	1.50	1.706	3.803	4.606
BCG	0.39	1.55	1.80	4.00	4.75

**Table-7**  
**Parameters for Permeability coefficient of NR/PEO block copolymers**

Adsorbent	P x 10 <sup>-4</sup> cm <sup>2</sup> min <sup>-1</sup>				
	BC-1	BC-2	BC-3	BC-4	BC-5
Water	0.60	69.46	81.14	122.19	1971.62
MG	0.54	57.61	81.43	187.56	1977.20
CV	0.54	58.56	79.76	184.77	1952.8
MB	0.49	60.55	74.34	157.42	1825.08
ST	0.54	76.10	80.28	205.24	1913.33
BCG	0.51	64.8	77.4	180.00	1807.61

Bulkier oxalate ion in MG with the envelope of water would be further away from the dye cation compared to the chloride anion and dye cations in ST and MB. Hence, even in terms of easier accessibility to the cation in MG would be expected to form CTC more effectively than MB and ST. Resonance stabilization of MB and ST, even if comparable, the bulkiness of ST could be viewed as a deterrent in the efficiency of CTC bond formation. ST is the bulkiest and hence its diffusion through the matrix would be subjected to steric hindrance by the segments.

**Permeability Coefficient:** The permeation of a penetrant into a polymer depends on the diffusivity as well as on the sorption of the penetrant. The permeability coefficient can be computed from the following mathematical expression (6).

$$P = D \times S \tag{6}$$

Permeability coefficients show the net effect of sorption and diffusion processes, that is how much diffusant diffuses through the polymer. The values of S and P are given in table 6 and 7.

Permeability coefficient of a polymer is influenced by the sorption and diffusion of the dye. Table 7 shows that diffusion exerts a greater influence except in the case of ST.

The diffusion coefficient (D) values sorption coefficients (S) and permeation coefficient (P) of BC-5 are the highest values of the five series, which is assigned to the largest number of EO units. In the array of core-shells the surface area of the coronas made of PEO chains, is the greatest for BC-5. The surface area decreases in the following order BC-5 > BC-4 > BC-3 > BC-2 > BC-1. Thus permeability will be of the same order as above. Besides, another common trend is that in each sample the BCG uptake is lowest of the five dyes and water. The general trend of

permeation in water and dyes is water ≥ MG > CV > MB < ST > BCG. Hence it seems that diffusivity exerts a greater influence than sorption in determining the trend of permeation.

### Conclusion

Block copolymers (BCs) of varying compositions were prepared from hydroxyl terminated liquid natural rubber (HTNR) and polyethylene oxide (PEO) of various molecular weights, by solution polymerisation. Two phase morphology of these NR/PEO BCs was confirmed by thermal studies and transmission electron microscopy analysis, in a previous paper of ours. The hydrophilic PEO, constituting the hard domains, confers on these BCs the ability to swell in water and in aqueous cationic dyes, viz., malachite green (MG), crystal violet (CV), safraninT (ST), methylene blue (MB) and bromocresol green (BCG). As the PEO content increased, the diffusion and permeation coefficients of BCs increases in the following order, viz., NR-b-PEO-2000 (BC-1) < NR-b-PEO-4000 (BC-2) < NR-b-PEO-6000 (BC-3) < NR-b-PEO-8000 (BC-4) < NR-b-PEO-10000 (BC-5). Variation of equilibrium swelling of the BCs in dyes also confirms the above order, which is chiefly due to the increasing number of ethylene oxide units, the lesser crosslink density and the greater molar mass between crosslinks as we traverse from NR/PEO-2000 to NR/PEO-10000 in the above series. Swelling studies also point to the fact that the order of interaction of the dyes or sorption with the BCs is MG > CV > ST > MB > BCG. Diffusional exponent value is Fickian in water and in dye solution for BC-1 and for the rest of the BCs it is anomalous type in water and in dye solutions. Hence it is inferred that the rate of chain relaxation is greater than the rate of diffusion in BC -1 during

swelling whereas in the others, rate of polymer chain relaxation and diffusion are similar.

The above results help surmise that NR/PEO hydrogels can be used as water retainers, for carrying some substances in aquatic fields involving environmental, pharmaceutical, agricultural and biomedical applications.

## Reference

1. Sanghi R., Bhattacharya B. and Singh V., Cassia angustifolia seed gum as an effective natural coagulant for decolourisation of dye solutions, *Green Chem.*, **4**, 252–254 (2002)
2. Namasivayam C., Arasi D.J.S.E. Removal of congo red from wastewater by adsorption onto waste red mud, *Chemosphere*, **34**, 401–417 (1997)
3. Moozyckine A.U., Davies D.M., Green S as a prototype for an environmentally-degradable dye: the concept of a green dye in future Green Chemistry, *Green Chem.*, **4**, 452–458, (2002)
4. Akhtar S., Khan A.A. and Husain Q., Potential of immobilized bitter gourd (*Momordica charantia*) preoxidases in the decolourization and removal of textile dyes from polluted wastewater and dyeing effluent, *Chemosphere*, **60**, 291–301 (2005)
5. Crini G., Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym. Sci.*, **30**, 38–70 (2005)
6. Senkal B.F. and Yavuz E., Preparation of poly (vinylpyrrolidone) grafted sulfonamide based polystyrene resin and its use for the removal of dye from water, *Polym. Adv. Tech.*, **17**, 928–931 (2006)
7. Hashem A., Abdel-Halim E.S., Socker H.H. Bi-functional starch composites prepared by gamma-irradiation for removal of anionic and cationic dyes from aqueous solutions, *Polym. Plast. Tech. Eng.*, **46**, 71–9 (2007)
8. Ohmine I., Tanaka T. Salt effects on the phase transition of ionic gels, *J. Chem. Phys.*, **77**, 5725–5729 (1982)
9. Katayama S., Hirokawa Y., Tanaka T. Reentrant phase transition in acrylamide-derivative copolymer gels, *Macromolecules*, **17**, 2641–2643 (1984)
10. Sibel Duran, Dilek Solpan, Olgun Guven, *Nucl. Instr. and Meth. In Phys. Res. B*, **151**, 196-199 (1999)
11. Gamze Guclu, Sibel Keles, *J. of Appl. Polym. Sci.*, **106**, 2422-2426 (2007)
12. Karadag E., Saraydin D. and Guven O. *J. of Appl. Polym. Sci.*, **61**, 2367-2372 (1996)
13. Zhang L.M., Zhou Y.J., Wang Y. Novel hydrogel composite for the removal of water-soluble cationic dye, *J. Chem. Tech. Biotech.*, **81**, 799–804 (2006)
14. Ravindran T., Nair M.R.G., Francis D.J., *J Appl Polym Sci*, **35**, 1227 (1988)
15. Chandrasekharan Nair R. Block Copolymers from liquid natural rubber and polyether. Ph.D thesis, 1998, School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India (1998)
16. Hadjichristidis N., Pispas N. and Floudas G., Block copolymers: Synthetic strategies, Physical Properties and Applications Wiley- Interscience (2003)